ENVIRONMENTAL ASSESSMENT OF ALKALI-CATALYSED BIODIESEL PROCESS USING WAR ALGORITHM

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ABSTRACT

A continuous homogenous chemical process flow sheet for biodiesel production from waste cooking oil under alkaline conditioning was developed. The process simulation was conducted by using Aspen Plus software simulator since it can optimize the simulation process. Details on the operating conditions and equipment designs for the process were obtained from the previous research. By defining suitable indicators from the result obtained, the potential environmental impact (PEI) of the process towards the environment can be conducted. Hence to determine the PEI value, WAR Algorithm is then introduced. It is used to evaluate the environmental friendliness of a process and was carried out by using the developed Microsoft Excel spread sheet. There are four PEI indexes involved (TRO, TOP, TRG and TGP) as the comparative manner. To evaluate in PEI indexes, eight PEI categories are used (HTPI, HTPE, ATP, TTP, GWP, PCOP and AP). The result of PEI value obtained was compared with the heterogeneous chemical process. As conclusion, heterogeneous catalysed is desirable chemical process since it was produced lower PEI value and had lower chemical impact towards the environment compared to homogenous chemical process.

PENILAIAN TERHADAP ALAM SEKITAR BERDASARKAN PROSES PEMANGKIN ALKALI BIODIESEL DENGAN MENGGUNAKAN WAR ALGORITHM

ABSTRAK

Sebuah pengeluaran prosess kimia homogen yang berterusan daripada minyak sayuran telah dibuat. Proses simulasi telah dijalankan dengan menggunakan perisian Aspen Plus kerana ia boleh mengoptimumkan proses simulasi. Keadaan proses operasi dan rekabentuk peralatan yang lengkap telah diambil daripada penyelidikan yang lepas. Dengan mendefinisikan petunjuk daripada keputusan yang diberikan, potensi impak alam sekitar (PEI) daripada proses kepada alam sekitar, telah diperkenalkan. Untuk mendapatkan nilai PEI, Algorithm WAR telah diperkenalkan. Untuk mengira tahap mesra alam proses tersebut, perisian Excel yang telah diformulasi telah digunakan. Terdapat empat indeks PEI yang terlibat (TRO, TOP, TRG dan TGP) sebagai perbandingan pengiraan. Untuk mengira indeks PEI, lapan PEI kategori telah digunakan (HTPI, HTPE, ATP, TTP, GWP, PCOP dan AP). Keputusan daripada nilai PEI yang dikeluarkan telah dibandingkan dengan proses kimia heterogen. Kesimpulannya, proses kimia heterogen adalah lebih baik kerana mempunyai nilai PEI yang rendah dan bahan kimia yang digunakan kurang memberi kesan kepada alam sekitar berbanding proses homogen.

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LIST OF ABBREVIATIONS

AP	Acidification Potential
ASTM	The American Society For Testing and Material
ATP	Aquatic Toxicity Potential
$C_{19}H_{36}O_2$	Methyl Oleate
$C_3H_8O_3$	Glycerol
$C_{57}H_{104}O_6$	Triolein
CH_4O	Methanol
CSTR	Continuous Stirred-Tank Reactor
FAME	Fatty Acid Methyl Ester
GWP	Global Warning Potential
H_2O	Water
H_2PO_4	Phosphoric Acid
HTPE	Human Toxicity Potential by Inhalation/ Dermal Exposure
HTPI	Human Toxicity Potential by Ingestion
MT	Metric tonne
Na_3PO_4	Sodium Phosphate Salt
NaOH	Sodium Hydroxide
ODP	Ozone Depletion Potential
PCOP	Photochemical Oxidation Potential
PEI	Potential Environmental Impact
PFD	Process Flow Diagram
TGP	Total Rate Generation/Product
TGR	Total Rate Generation
TOP	Total Rate Output/Product
TOR	Total Rate Output
TTP	Terrestrial Toxicity Potential
WAR	Waste Reduction Algorithm

CHAPTER 1

INTRODUCTION

1.1 Background of Proposed Study

As stated by Banarjee and Chakraborty (2009), high consumption of diesel used in transport can lead towards major deficit of the resources in future. Therefore, other alternatives should be taken as the replacement. Recently, researchers have been found that there are many resources can be used as the alternatives. Here, the usage of biodiesel considered as the replacement recently. Lam *et al.,* (2009) defined biodiesel as the transesterification reaction of triglycerol with alcohol to produce fatty acid methyl ester and glycerol as the byproduct. In this research we are interested to used waste cooking oil as raw material because of the low cost consumption. Beside, alkali catalysed reaction system is choose because of its transesterification reaction is more rapid than acid catalysed reaction (Zhang, 2002). Later on, production of 8000 MT/annum of biodiesel will be simulated by using Aspen Plus software simulator. Othman (2011) stated that the basic steps involved in

process simulation are defining chemical components, selecting thermodynamic model and method, designing process flowsheet by choosing proper operating units, determining plant capacity, and setting up input parameters. Then, in order to describe the flow and the generation of potential environmental impact through a chemical process, the Waste Reduction Algorithm (WAR) has been developed (Young *et al.*, 2000). WAR algorithm is based on the conventional mass and energy balance from the process or Potential Environmental Impact. The lowest PEI value is preferable.

1.2 Problem Statement

Recently, the production of biodiesel seems significant due to the decreasing of the sources of diesel. However, the high emission of chemical; from chemical process design actually could lead towards health and environmental problem. Hence, the simulation of biodiesel production and environmental assessment of the process must be conducted.

1.3 Research Objective

1.3.1 To simulate and modeling the biodiesel production from alkali catalysed transesterification of waste cooking oil by using Aspen Plus.

1.3.2 To perfom the environment analysis of biodiesel production from vegetable oil using WAR algorithm.

1.4 Scope of Proposed Study

We need to perform simulation and modeling of biodiesel production from virgin vegetable oil. Later on, the research will proceed to the environmental analysis of the process by using WAR algorithm.

1.5 Significance of Proposed Study

By conducting this research, a model of biodiesel production from waste cooking oil can be generated. From the simulation result, the environmental analysis of the process also will be conducted by using WAR algorithm method. Hopefully by this research, the result obtained can open the new paradigm of engineers by bringing another perspective in analyse the process design.

1.6 Thesis Outline

In this chapter we are focusing on the general background of the research, problem statement, research objective, scope of proposed study, expected outcome, and also the significance of the proposed study. The next chapter will discuss further on the literature review of the simulation process together with the environmental assessment of the process design.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Biodiesel

Lam, Lee and Mohamed (2010) stated that the consumption of diesel fuel is increasing from days to days. It is estimated that the world wide's consumption of biodiesel especially in transport usage is nearly achieved until 934 million tonnes per year. The huge consumption by mankind can make the natural resources will be deficit in future (Banerjee *et al.,* 2009). Besides, the high usage of diesel can cause the greenhouse effect increase significantly resulting from the high emission of carbon monoxide to the air. Because of it, some other alternatives rather need to be replaced in order to full fill the mankind demanding beside yet keep the positive

environment values (Zhang *et al.*, 2003a). Hence because of these factors, biodiesel is introduced as the replacement.

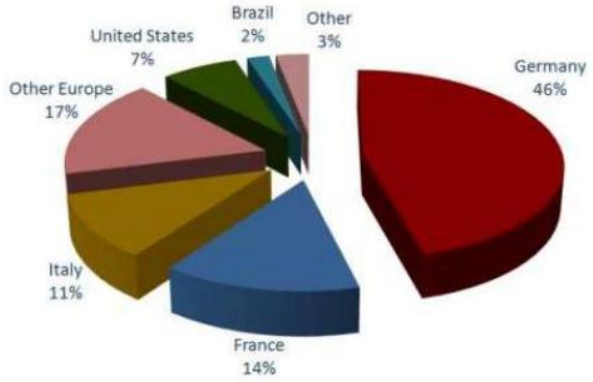

Figure 2.1 World production of biodiesel
(Source: Guerro, Romerro & Sierra, 2005)

As defined by The American Society for Testing and Materials (ASTM), biodiesel fuel is a mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock. The raw materials of biodiesel can be vegetable oil, animal fats, canola seeds and many organic and any biodegradable sources (Rice, Frohlich & Korbitz, 1997). However, the expensive raw material is the great barrier in the production of biodiesel. As reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw material (Ariffin, 2009). Hence, waste cooking oil is used as the interest because it is having low cost of material and can reduce to almost zero (Zhang, 2002).

Besides, Jacobson et al (2008) also stated that the usage waste cooking oil as biodiesel actually can reduce the environmental pollution by disposed it. Currently large quantity of waste cooking oil can be easily obtained from household and restaurants. ‘Thus, waste cooking oil offers significant potential as an alternative

low–cost biodiesel feedstock which could partly decrease the dependency on petroleum-based fuel' (Jacobson, 2008).

Table 2.1 Physical and chemical properties of biodiesel (Source: American Standard Test Material, 2001)

Vegetable oil methyl ester	Kinematic viscosity (mm^2/s)	Cetane number	Lower heating value (MJ/l)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt %)
Peanut[a]	4.9 (37.8°C)	54.00	33.60	5.00	176.00	0.88	-
Soybean[a]	4.5 (37.8°C)	45.00	33.50	1.00	178.00	0.89	-
Soybean[b]	4.0 (40°C)	45.7-56	32.70	-	-	0.880 (15°C)	-
Babassu[a]	3.6 (37.8°C)	63.00	31.80	4.00	127.00	0.88	-
Palm[a]	5.7 (37.8°C)	62.00	33.50	13.00	164.00	0.88	-
Palm[b]	4.3-4.5 (40°C)	64.3-70	32.40	-	-	0.872-0.877 (15°C)	-
Sunflower[a]	4.6 (37.8°C)	49.00	33.50	1.00	183.00	0.86	-
Tallow[a]	-	-	-	12.00	96.00	-	-
Rapeseed[b]	4.2 (40°C)	51-59.7	32.80	-	-	0.882 (15°C)	-
Used rapeseed[c]	9.48 (30°C)	53.00	36.70	-	192.00	0.90	0.00
Used corn oil[c]	6.23 (30°C)	63.90	42.30	-	166.00	0.88	0.00
Diesel fuel[b]	12-3.5 (40°C)	51.00	35.50	-	-	0.830-0.840 (15°C)	-
JIS-2D[c] (Gas oil)	2.8 (30°C)	58.00	42.70	-	59.00	0.83	0.05

[a] Ref.10.
[b] Ref. 20.
[c] Ref. 19.

Later, in order to convert the raw materials to the main product, catalysed transesterification reaction has been proposed. Zhang (2002) claimed that it is called 'transesterification' because it is involving the conversion of one ester (triglyceride) to another ester (alkyl ester) with a presence of catalyst. In this research proposal, we are interested to focus on the homogenous catalysis reaction because it provides

much faster reaction rates compared to the heterogeneous catalyst reaction (Arifin, 2009).

2.2 Process Description

Transesterification process is the most common process that used to yield the biodiesel. It is a catalysed chemical reaction which involved the triglyceride and an alcohol to produced fatty acid methyl ester (FAME) with glycerol as the byproduct (Wang, Ou, Liu, Xue & Tang, 2006). In order to produce the highest conversion of FAME, large amount of methanol is used as the solvent. Instead of other alcohol, methanol is commonly used due to its low cost and easy to get (Zhang *et al.*, 2003a; Zhang *et al.*, 2003b).

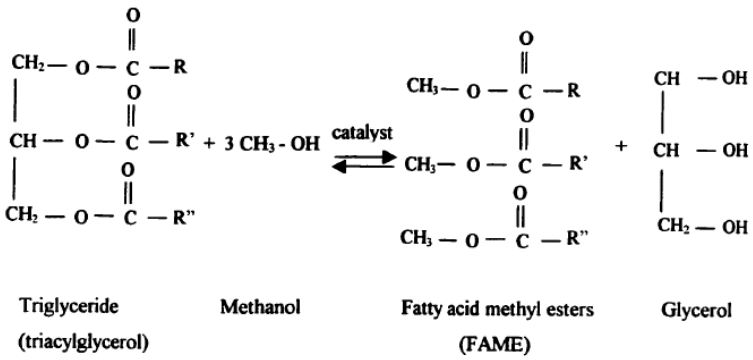

Figure 2.2 The transesterification of triglyceride with methanol to produce fatty acid methyl esters
(source: Zhang, 2002)

Homogenous catalysed reaction is used because it produced high conversion of product in shorter time. It is also provides faster reaction rate compared to heterogenous catalysed reaction (Lam *et al.,* 2010; Ariffin, 2009). Instead of types of phases, transesterification reactions also can be either alkali catalysed, acid catalysed or enzyme catalysed (Zhang *et al.,* 2003a). However, alkali catalysed is the most preferable one because its transesterification reaction was more rapid than the acid catalysed reaction (Zhang, 2002). Due to this reason, together with the fact that the alkaline catalysts are less corrosive that acidic compounds, industrial processes usually favour base catalyst such as alkaline metal alkoxides, and hydroxides, as well as sodium and potassium carbonates (Braz, 1998).

For basic catalyst, alcohol-oil molar ratio 6:1 is the most used ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol (Khalid 2011). Under this condition, conversion of oil to esters could reach 95% within one hour. The construction material for the process equipment in the alkali catalysed system is also important. Zhang (2002) stated that the alkali catalysed transesterification was less corrosive to process equipment than the acid catalysed process.

Helwani, *et.al.,* (2009) stated that normally, the alkaline catalyst show high performance when vegetable oil with high quality is used. However, when the oils contain significant amounts of free fatty acids, they cannot be converted into biodiesels but to a lot of soap. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of biodiesel, glycerine and wash water. Triglycerides are readily transesterified batch wise in the presence of alkaline catalyst at atmospheric pressure and at a temperature of approximately 60–70 ° C with an excess of methanol. It often takes at least several hours to ensure the alkali

(NaOH or KOH) catalytic transesterification reaction is complete. The removal of these catalysts is technically difficult and it brings extra cost to the final product. Because of it, the reaction of free fatty acid with alkaline catalyst will not be considered in this research.

Table 2.2 Fatty acid composition for various feedstock (source: Othman, 2011)

Vegetable oil	Fatty acid composition % by weight									Acid value	Phos (ppm)	Peroxide value
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3			
Corn	11,67	1,85	0,24	0,00	0,00	26,16	0,00	60,60	0,48	0,11	7	18,4
Cottonseed	28,33	0,89	0,00	0,00	0,00	13,27	0,00	57,51	0,00	0,07	8	64,8
Crambe	20,7	0,70	2,09	0,80	1,12	18,86	58,51	9,00	6,85	0,36	12	26,5
Peanut	11,38	2,39	1,32	2,52	1,23	48,28	0,00	31.95	0.93	0,20	9	82,7
Rapeseed	3,49	0,85	0,00	0,00	0,00	64,4	0,00	22,30	8,23	1,14	18	30,2

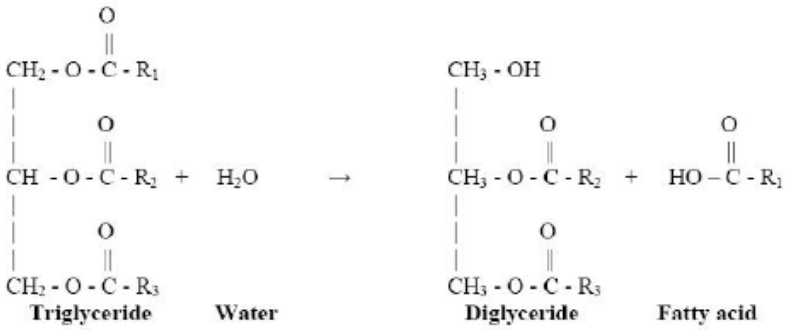

Figure 2.3 FFA formation with presence of water (source: Othman, 2011)

Zhang *et al.*, (2003a) stated that a 6:1 molar ratio of alcohol to oil was recommended at a temperature which is near to the boiling point of methanol. Based on this ratio, about 90-98% of oil conversion to methyl esters was observed within 90 min. The oil and a mixture of methanol and sodium hydroxide were fed into the transesterification reactor. Inside the reactor, the temperature and pressure of the process was set at 60^{o}C and 1 bar respectively (Othman, 2011).

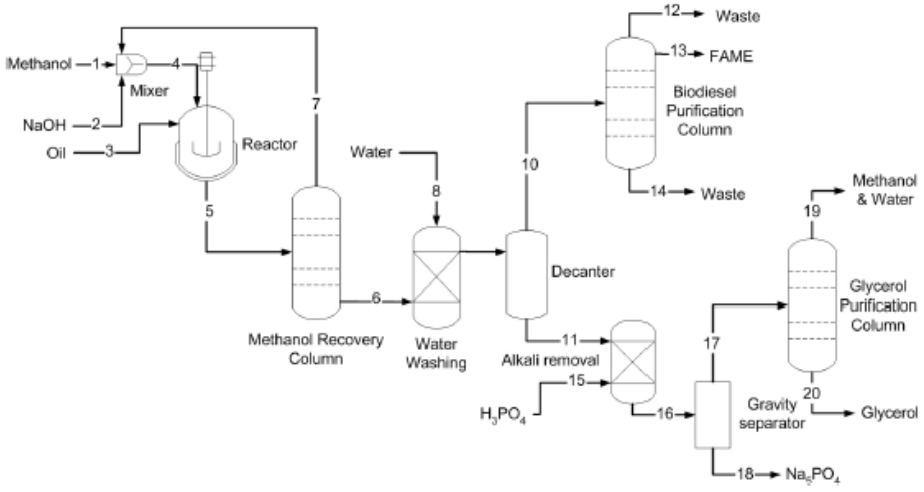

Figure 2.4 Biodiesel flowsheet (alkali based transesterification) (source: Othman, 2011)

Zhang *et al.*, (2003a & 2003b) also claimed that an effluent stream of the transesterification reactor is contained FAME, glycerol, methanol, unconverted oil and sodium hydroxide. Then, they were entered methanol distillation column by setting 100% distillate rate of methanol. The distilled methanol mixed with the fresh methanol stream, then proceeded to the reactor. In order to purify the product, a multi-stage water washing was employed in the process (Zhang *et al.,* 2003a). Cited by Zhang (2002), using the waste water washing at 50^{o}C was the best way to separate and purify the biodiesel product. The effluent product was then forwarded to a distillation column to further remove methanol and water.

From the top of the column, high purity FAME was obtained in the distillate. The bottom stream of the water washing column, containing sodium hydroxide, glycerol, methanol, and water were entering the neutralization reactor to remove the catalyst (sodium hydroxide) by adding phosphoric acid (Zhang *et al.*, 2003b). To

remove the excess alkali catalyst, neutralization reactor was used by adding phosphoric acid into the feed reactor. From the reaction, Na_5PO_4 solid was produced. The neutralization reaction below was followed:

$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$$

After the sodium is removed, the stream was then sent to gravity separator to separate the solid sodium phosphate salt (Othman, 2011). Then, liquid stream was proceeded into glycerol purification column where the bottom stream contained high quality byproduct (glycerine).

However, some process assessment will be discussed in the next topic in order to verify whether these factors having significant impact towards on acid catalysed reaction process of biodiesel production.

2.3 Process Assessment

In sustainability assessment, environmental analysis is one of the crucial assessments in a plant design. The environmental analysis of the alkali transesterification of biodiesel production from waste cooking oil will be conducted later on in order to explore the impact the biodiesel manufacture towards the environment.

2.3.1 Environmental Assessment

Young and Cabezas (1999) stated that the concept of implementing pollution prevention techniques into process design has received more attention in recent years. Hence, environmental analysis is also conducted in this research. This is to make sure that the sustainable biodiesel strategy is followed, which to ensures that biofuels are produced and consumed in a sustainable manner, as well as the environmental (Zyl & Barbour, 2010). Recently, there too many massive growth of plant company that very success in their products. However later, they could not realised that actually the process reaction that produced by them can lead towards the decreasing of environmental value (Othman, 2011).

So here, Waste Reduction algorithm (WAR algorithm) is being used in order to investigate the life cycle assessment and also assessment of waste reduction from the acid catalysed reaction process. The WAR algorithm is simply a tool to be used by design engineers to aid in evaluating the environmental friendliness of a process (Young *et al.,* 2009). WAR algorithm is first introduced by Young and Cabezas in 1999 but 'the concept of pollution prevention was first presented in the 1970s via heat exchange networks (HENs) which first introduced by El-Halwagi and Manou-Siouthakis'(Young, Scharp & Cabezas 2000).

Young *et al.,* (2000) also claimed that the WAR algorithm is a methodology used to evaluate the relative environmental impact of a chemical process. It will consider only the manufacturing aspect of product's life cycle. From Potential Environmental Impact (PEI) balance, 'PEI indexes are calculated which provide a

relative indication of the environmental friendliness or unfriendliness of the chemical process' (Young *et al.*, 2000).

This kind of algorithm is rather to be used because it is deal with the component-specific potential environment impact (PEI). PEI is based on the conventional mass and energy balance which is conducted at the manufacturing level (Othman, 2011). Here, 'PEI indexes are calculated which provide a relative indication of the environmental friendliness or unfriendliness of the chemical process' (Young *et al.*, 2000)

The following equation will be used in this research in order to determine the environmental impact from the process (Othman, 2011; Young *et al.*, 2000).

$$I_{gen}^{t} = I_{out}^{cp} - I_{in}^{cp} + I_{out}^{ep} - I_{in}^{ep} \tag{2.1}$$

Then, for the mass expression below equation will used

$$I_{in}^{cp} = \sum_{h}^{Streams} \sum_{c}^{Comps} M_{h,in} \sum_{c}^{Comp} \left(x_{c,h}\psi_{c,i}^{s}\right) \tag{2.2}$$

$$I_{out}^{cp} = \sum_{h}^{Streams} \sum_{c}^{Comps} M_{h,out} \sum_{c}^{Comp} \left(x_{c,h}\psi_{c,i}^{s}\right) \tag{2.3}$$

Where I_{in}^{cp} is the potential environment impact of the energy conversion process while I_{out}^{cp} is the summation of all gaseous output stream. The unit used is PEI/h. To calculate the product basis PEI/kg, following formula is being used.

$$\hat{I}^{t}_{gen} = \frac{I^{cp}_{out} - I^{cp}_{in} + I^{ep}_{out}}{\sum M_p} \quad (2.4)$$

$$\hat{I}^{t}_{out} = \frac{I^{cp}_{out} + I^{cp}_{out}}{\sum M_p} \quad (2.5)$$

All the formulas that will be used are included all the products and non-product streams. High value of PEI is not considerable because the lower the PEI values the desirable the process (Othman 2011)

The TRO values that generated in Microsoft Excel flow sheet is based on the specific PEI of each chemical over certain impact category. The indicators that involved in this impact factors are human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation/dermal exposure (HTPE), aquatic toxicity potential (ATP), terrestrial toxicity potential (TTP), global warning potential (GWP), photochemical oxidation (smog formation) potential (PCOP), acidification potential (AP) and ozone depletion potential (ODP).

Table 2.3 Impact factors (process) for each component (Othman, 2011)

No.	Component	HTPI	HTPE	ATP	TTP	GWP	PCOP	AP	ODP
		LD50	TWA-TLV	LC50	LD50				
1	TG	0	0	0	0	0	0	0	0
2	MEOH	5628	200	29400	5628	0	0.123	0	0
3	NAOH	0	2	0	0	0	0	0	0
4	GLY	12600	10	58.5	12600	0	0	0	0
5	FAME	0	0	0	0	0	0.223	0	0
6	WATER	0	0	0	0	0	0	0	0
7	H3PO4	1530	1	0	1530	0	0	0	0
8	NA3PO4	4150	15	220	4150	0	0	0	0

2.4 Concluding Remark

In conclusion, there are many routes that be used in order to produced biodiesel from waste cooking oil. But as stated above, homogenous alkali catalysed reaction processes is the most preferable one. This is due to the most economic process compared to others. The environmental analysis of the process also will be performed later on. For the next chapter, we will discuss more on methodology of the research so that we can have a clearer vision on how this research will be conducted.